FIRST SEMIANNUAL TECHNICAL REPORT

STRUCTURAL EFFECTS ON ELECTRICAL PROPERTIES
IN AMORPHOUS SEMICONDUCTING MATERIALS

VANDERBILT UNIVERSITY

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STRUCTURAL EFFECTS ON ELECTRICAL PROPERTIES

IN AMORPHOUS SEMICONDUCTORS


SCHOOL OF ENGINEERING

VANDERBILT UNIVERSITY

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# ABSTRACT

During this report period, work has been concentrated on a survey of the structure, electrical and magnetic properties of transition metal oxide-phosphate glasses and glasses in the $As_2Te_3$-$As_2Se_3$ system which possess electrical or magnetic device potential. Results of magnetic and electrical observations in an $FeO$-$P_2O_5$ glass have revealed a surprisingly high degree of magnetic and structural order.

Examination of a $V_2O_5$ - $P_2O_5$ glass has revealed a "Phase transition" in the glass at a low temperature. Initial results on a $CuO$-$P_2O_5$ glass are promising, in that an extremely conductive film has been observed and bulk conduction of the same magnitude will be potentially useful in device applications.

Work in the $As_2Te_3$-$As_2Se_3$ system has shown switching behavior which can be controlled with compositional variation. This material has also been used as a circuit element for a microwave oscillator which has operated in a transient mode at 5 GHz.

## STATEMENT OF PROBLEM

The device potential in amorphous semiconducting materials is a largely unexploited area, despite considerable research in this field. This is the result of a lack of systematic structure-property oriented research in these materials. A fundamental understanding of the structural features of this class of materials will allow rational interpretation and control of relationships between glass preparation variables and important electrical and magnetic properties.

Electronic conduction in amorphous solids has become the subject of interest to a number of theoreticians and has been reviewed by Mott (1), Gubanov (2) and numerous others. Virtually all of these works have begun with an assumption that amorphous solids are uniformly random, even though they recognize glasses are generally heterogenous. These results of the theoreticians have developed analytical descriptions of several systems which have been experimentally verified in some cases. Attempts to extend this approach to microscopically heterogenous systems have yielded very little information. There remains a considerable body of results, including Hall and Seebeck coefficients, which are not rationalized by present theory.

Pearson (3) has suggested that heterogenous structure in these materials may explain these anomalies if the separated phase is crystalline. It appears that heterogenous

transport analysis similar to that of Volger (4) or Bube (5)
is required to ascertain the transport behavior in each phase.

Another important anomaly between theory and observation
concerns the theoretically predicted insensitivity of amor-
phous semiconductors to doping.  Early experimental obser-
vations by Kolimets, et.al. (6), confirmed the theoretical
prediction, but recent work by Mackenzie (7) seems to con-
flict with theory and the early work.  It appears that
the above anomalies are the result of inadequate structural
characterization, rather than fundamental theoretical
problems.

Further evidence that structural heterogenities lie at
the root of these anomalies can be inferred from work by
Kinser, et.al. (8), in $K_2O-P_2O_5-V_2O_5$ glasses.  This work has
shown that marked changes in dielectric behavior occur
during thermal treatments customarily used to stress relieve
glasses.  These changes have been shown to be the result of
structural changes involving precipitation of small amounts
of crystals.

Wilson and Kinser (9) have observed similar, but some-
what more complex, behavior in $FeO-P_2O_5$ glasses after thermal
treatments corresponding to annealing.  Electron spin re-
sonance (ESR) results have shown the onset of structural
changes during thermal treatment prior to their observation

by other commonly employed techniques.

It is thus apparent that homogenous glasses, semi-conducting or otherwise, are the exception rather than the rule.

## GENERAL METHODOLOGY

The electrical and magnetic property changes accompanying structural modifications during glass processing are of prime interest in the present work. The above questions can only be answered with detailed structural characterization of representative glasses from the oxide and chalcogenide groups. The initial oxide glass examined was the 55 FeO-45 $P_2O_5$ glass along with glasses from the $V_2O_5$-$P_2O_5$, $CuO$-$P_2O_5$ and $TiO_2$-$P_2O_5$ systems. The initial chalcogenide glasses are from the $As_2Te_3$-$As_2Se_3$ system.

Structural characterization of these systems is being accomplished using electron microscopy, Guinier-DeWolff x-ray, electron spin resonance spectroscopy, magnetic susceptibility, electron microprobe, and dielectric relaxation techniques.

In conjunction with the structural tools, it is necessary that the conductivity, switching behavior and Seebeck co-efficient be monitored to allow direct structure-property correlations.

RESULTS

## Oxide Systems

### Glass Formation in Transition Metal-Phosphates

One of the initial efforts during this report period has been a survey of the glass-forming tendencies in the various transition metal oxide phosphate systems. This work has yielded binary glasses of $TiO_2$, $CuO$, $CoO$, $MnO_2$, $V_2O_5$, $ZnO$ and $FeO-P_2O_5$. The CoO, MnO and CuO glasses appear to be entirely new glasses, in that no mention of their preparation is known in the literature. Efforts to prepare $Cr_2O_2$ and NiO glasses were partially successful, but these glasses contained some crystals.

### $FeO-P_2O_5$ Glasses

Electrical properties of the 55 $FeO-45P_2O_5$ glass with varying $Fe^3$/Fe total ratio have been extensively studied. These results are contained in a thesis and an abstract is included in Appendix A. These glasses devitrify during thermal treatments, and the electrical property changes observed indicate that:

1. At least two crystalline phases grow during thermal treatments incorporating first $Fe^{3+}$ and subsequently $Fe^{2+}$.

2. Dielectric loss behavior indicates that the two types of crystals have either different morphology and/or different

electrical conductivity.

3. Glasses with high $Fe^3/Fe$ total ratios exhibit a much higher tendency to crystallize, and hence are more subject to structural modifications.

The magnetic properties of this glass have also been examined; these results are contained in a paper which is included as Appendix B. Among the conclusions of this work are the observation that the major portion of the iron ions are antiferromagnetically ordered. This gives an extremely small magnetic effect, and we interpret it as indicating a structural ordering of iron ions in the glass. This indicates that the short range order in the glass is considerably higher than that which a random phosphate network with a high modifier content would seem to allow.

In summary, the magnetic observations of coupling between iron ions supports the electron hopping theory of conduction. It also tends to indicate the considerable structural order is present.

## $V_2O_5-P_2O_5$ Glasses

Magnetic observations of $V_2O_5-P_2O_5$ glasses have revealed a phenomena similar to a magnetic phase transition at low temperatures. These results are summarized in an abstract attached as Appendix C. These glasses exhibit inflections in electrical behavior at temperatures near the magnetic transition temperatures, although our electrical data at these temperatures is somewhat suspect. This behavior is nontheless

real and indicates what appears to be a "phase transition" in a glassy material.

Recently published electrical data by Linsley, et.al.(10), on this system supports our observations. Their data indicates a pronounced change in activation energy for electrical conductivity in the temperature range (around -70°C) where the magnetic transition occurs.

The structural implications of the above observations are currently under examination, but at present we do not wish to speculate on these observations.

## $CuO-P_2O_5$ Glasses

The initial preparation of $CuO-P_2O_5$ glasses indicated that this glass has unique properties. The 55 $CuO-45P_2O_5$ glass initially melted exhibited a copper colored external layer which evidently resulted from a change in the oxidation state at the surface during cooling. The thin surface layer exhibited an almost metallic conductivity (approx. $10^2$ohm-cm), while the bulk glass was more resistive. Subsequent to this observation, several additional glasses were melted using $CuO_2$ and CuO to vary the oxidation state. It now appears that with appropriate oxidation tate control the high conductivity surface layer can be made a bulk feature of these glasses. It has already been possible to increase the bulk

conductivity by two orders of magnitude using $Cu_2O$ with no attempt at atmosphere control.

Survey ESR data on these glasses indicates that the spectra is complex, and we have not attempted to analyze it in detail. The potential of this system appears to be extremely good because of the very wide range of conductivities attainable.

## $TiO_2-P_2O_5$ Glasses

The preparation of a $55TiO_2-45P_2O_5$ glass using the conventional air melting in silica crucible process was unsuccessful because the $P_2O_5$ volatilized before reaction with the $TiO_2$. The results of Tien (11) in a 5 $TiO_2-2$ $P_2O_5$ glass have just recently appeared and enable us to surmount the above problem. The 5:2 glass was prepared by prereacting $TiO_2$ with aqueous $H_3PO_4$ and subsequently drying prior to melting. This technique produced useable samples which are at the moment being examined. The magnetic susceptibility apparatus for this work is in house and will be operational early in the next report period.

### Glass Preparation

## $As_2Te_3-As_2Se_3$ Glasses

Glasses from the system x $As_2Te_3-(1-x)As_2Se_3$ have been prepared by melting reagent grade materials in evacuated and sealed Vycor tubes. The tubes were placed in a specially

designed "rocking furance" at 800°C for one hour and sub-
sequently quenched in room temperature water. Compositions
with $As_2Te_3/As_2Se_3$ ratios 1.00, 0.80, 0.70, 0.50, 0.40 and
0 have been prepared. Electrical samples of the above com-
positions were made by rapidly heating the random lumps of
glass on a graphite block and pressing with a second block
to make a small button. These samples were then ground and
polished for electrical measurements.

## X-Ray and Electron Microscopy

One of each of the samples above was examined in the
Guinier-DeWolff x-ray camera to determine its state. With
the exception of the pure $As_2Te_3$, all of the samples were
non crystalline (less than 0.5 wt.% crystal). The $As_2Te_3$
was crystalline, as anticipated, and is presently being
indexed for later comparison with thermally treated glasses.

When the 0.80 glass was examined by replica electron
microscopy, evidence of phase separation was observed.
The structure has not been fully characterized, but it
contains separated regions characteristic of a spinodal
decomposition.

## Dielectric Loss Behavior

A sample of the 0.8 glass has also been examined using
dielectric relaxation techniques. These results do not
show evidence of dielectric loss maxima, except at un-
resolved low frequencies. This investigation is being pursued,

and thermally treated samples are being prepared for examination.

## Switching Behavior

The memory/threshold switching behavior of the 0.8 $As_2Te_3$ glass has been extensively studied and is the subject of a paper included as Appendix D. This work has shown that these glasses switch with unusually small applied fields and can be made to behave as either memory or threshold devices. The critical voltage for switching has been shown to be independent of sample thickness.

Other work not reported in Appendix D has focused on the compositional behavior of the switching voltage and the two negative resistance regions. These preliminary results appear to strengthen the arguments for thermally induced phase transitions in these glasses. DTA and calorimetric data are being obtained to strengthen the preliminary conclusions above. The phase transition is also supported by the observation that the critical switching voltage increases as composition moves toward $As_2Se_3$. The $As_2Se_3$, which is difficult or impossible to crystallize from the glass, has not been switched even at 1,000 volts.

## Microwave Observations

A microwave diode has been prepared using the 0.8 $As_2Te_3/As_2Se_3$ glass and has been tested in a negative

resistance amplifier configuration at 5 GHz. Some difficulty was encountered in stabilizing the diode in its negative resistance region, but bursts of oscillation at 5 GHz have been observed for sustained periods of approximately 1 second. Since these very preliminary results, the work described in Appendix D has proposed an explanation of the negative resistance region which offers a firm theoretical basis for continuance in this area. A second diode designed for reduced loss at microwave frequencies is presently being fabricated.

## RECOMMENDATIONS

1.  It is our principal recommendation that this research be continued in its present direction.  It is anticipated that electron microscopy of these systems will be expanded in considerable detail.

2.  Our systematic approach, which consists of preparing numerous transition metal oxide-phosphate glasses, has yielded several unique glasses which deserve further study,  For example, the $CuO-P_2O_5$ glass has high electrical conductivity and is a good candidate for possible device application.

3.  The progress in stabilizing the negative resistance region by changing composition in the binary glasses should be pursued with an eye to further exploiting the structural variables which have given this improvement.

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# CORRELATIONS BETWEEN STRUCTURE AND ELECTRICAL PROPERTIES IN A 55a/o FeO--45a/o $P_2O_5$ GLASS

## ANDREW WINFIELD DOZIER

Thesis under the direction of Professor Donald L. Kinser

The tan $\delta_{A.C.}$ dielectric loss parameter as a function of frequency and D.C. resistivity vs. 1/T were measured on a 55a/o FeO--45a/o $P_2O_5$ glass as a function of heat treatment time at 600°C. The oxidation state of the Fe cations was varied in the specimens by adding dextrose to the melt. The as cast D.C. resistivity at 200°C increased with increasing $Fe^{3+}/Fe^{Tot}$ over the ranges in the ranges of this ratio which could be produced. A correlation was established between the behavior of the D.C. resistivity vs. 1/T with varying heat treatment times and the appearance of a high and lower frequency dispersion in the tan $\delta_{A.C.}$ vs. frequency measurements. A theory explaining this correlation is proposed and evidence in support of this theory obtained from Guinier DeWolff powder camera data.

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Electrical Conductivity and Magnetic Resonance
Correlations in Transition Metal Oxide-Phosphate
Glasses.* L. K. WILSON and D. L. KINSER, Vanderbilt
Univ.--The D. C. conductivity and magnetic resonance
spectra of several transition metal oxide-phosphate
glasses have been examined as a function of temperature.
The magnetic studies of the glasses revealed antiferro-
magnetic behavior with some similarity to the antiferro-
magnetism observed in the crystalline phases of the cor-
responding transition metal oxides. The electrical con-
ductivity of the glasses exhibit subtle changes at tem-
peratures corresponding to the magnetic transition tem-
peratures. These observations have been interpreted in
terms of the similarity of the short range order of the
glasses and crystalline phases.

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LOW-FIELD SWITCHING AND MEMORY PHENOMENA
IN AN AMORPHOUS SEMICONDUCTOR

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## INTRODUCTION

Beginning with the work of Ovshinsky in 1967 (1), considerable re-
search has been directed toward the understanding and utilization
of amorphous (chalcogenide) semiconducting materials (2,3,4). One
promising application of the amorphous semiconductor is memory
switching. This paper describes some experimental studies of
switching phenomena in the amorphous system 80 $As_2Te_3$:20 $As_2Se_3$.

## EXPERIMENTAL

The samples used in this experimental work were wafers with a
thickness of between 0.4 and 1.7 mm. Measurements were made on a
sample by sandwiching it between two brass electrodes in a holding
device designed to maintain constant contact pressure. Microscopic
examination of the sample surface was made before and after it
had been subjected to breakdown.

In order to observe the negative resistance transition between the
high and the low resistance states of the devices, it is necessary
to have a source of internal impedance greater than the magnitude
of the negative resistance. This condition was satisfied by using
a closed-loop voltage-controlled constant current source whose DC
output impedance was in excess of 15 megohms. The high source
impedance was also useful in eliminating the tendency of some samples
to switch at a high rate between states of different current. The
stability of the closed-loop system eliminated thermal hysteresis in
the I-V sweeps caused by heating of the output transistors. The
constant current circuit was designed to provide currents of 0-100
ma over a dynamic output voltage range of 0-250 V.

The I-V characteristics shown in Figures 1,2,3 and 4 were obtained
by driving the constant current circuit with a clamped sawtooth
wave. If the magnitude of the sweep was sufficiently small, the volt-
age never reached the breakdown value and the sample remained in
the high resistance state, as shown in Fig. 1. The value of re-
sistance in this state was normally in the megohm region, although
on occasion, after several cycles of breakdown, the value of the
off resistance might drop to 10-20 $K\Omega$. This situation was never
permanent, however, for the sample would always return in time to
the high resistance off state. The sample would remain in the high
resistance state indefinitely if not subjected to a breakdown volt-
age. Figure 2 shows the I-V characteristics for a considerably

larger sweep amplitude. Beyond some critical threshold voltage, $V_{br}$, the sample breaks down and passes through a negative resistance region consisting of two distinct parts. As the sweep current decreases, the sample initially returns along a low resistance path until a threshold current value $I_{th}$ is reached, below which the sample returns to the initial high resistance state. Because of the required holding current for the device to remain in the low resistance state, this type of behavior is known as threshold switching. Normally, the sample would continue to cycle in this manner indefinitely. However, a sufficiently slow return sweep rate often leads to a one-cycle sweep of the type shown in Figure 3. Here the sample remains in the low resistance state as the sweep current is reduced to zero, and will exhibit the low resistance characteristics of Figure 4 for future sweeps. This phenomenon is known as "memory switching" since the sample remembers the state in which it is left. A return to the high resistance state can be effected by pulsing the sample with a high current (50-100 ma) pulse of several milleseconds duration.

Initial efforts to determine the breakdown voltages of the devices were unsuccessful. A given sample would exhibit breakdown voltages over a range of 5 to 200 V., with a more or less random distribution within this range. To aid in the analysis of this inconsistency, a computer program was written which would plot a histogram of the number of breakdowns vs voltage and which was also able to produce the histogram with various degrees of statistical smoothing. The mean value and standard deviation of the original and smoothed histograms were calculated and were used as a measure of the validity of the smoothing technique. The program also calculated the mean and the standard deviation of the initial data set. The standard deviation of the data was taken as a measure of the data taking technique, with the assumption that a valid set of data should have a small standard deviation. The final program function was to produce a heavily smoothed time plot of the data. A highly erratic time plot was taken as an indication of poor data. Use of the program in conjunction with various data taking techniques produced a steady improvement in data until the point was reached where a consistent characterization of the device could be obtained. The improvement is evident in the fact that the initial data set had a mean of 48 V with a standard deviation of 36.4 V while a data set taken using improved techniques yielded a mean value of 100 V with a standard deviation of 5.6. The breakdown voltage was found to be virtually independent of the sample thickness.

## DISCUSSION

$As_2Se_3$ is a glassy material and has a low tendency to crystallize when cooled from the liquid phase. Samples of $As_2Se_3$ have been subjected to voltages as high as 1 kv without breaking down. Pure $As_2Te_3$, on the other hand, does not form a glass and accordingly has a very high conductivity. The system $As_2Te_3:20\ As_2Se_3$ can be prepared in a glassy state, the presence of the selenium being

sufficient to stabilize the glass. However, all evidence indi-
cates that the $As_2Se_3$ does not take place in the switching
mechanism. Rather, by forming a glass with a high $As_2Te_3$ content,
the $As_2Se_3$ sets up the conditions necessary for the switching
process to occur.

Tanaka et al (5) have studied the properties of the glass $As_{40}$
$Te_{50}Ge_{10}$, in which the germanium appears to play a role similar
to that of the selenium in the 80 $As_2Te_3$:20 $As_2Se_3$. Results of
their calorimetric data are shown in Figure 5. The material,
initially in a glassy state, is heated at a constant rate. At
temperature $T_1$, an exothermic reaction occurs which indicates
crystallization of the material. At the higher temperature $T_2$,
an endothermic reaction occurs, above which the material is liquid.
Once in the liquid state, cooling will cause the material to re-
turn to the glassy state, if rapidly cooled, or the crystalline
state, if cooled slowly. Further studies on the crystalline state
of the material indicated that the crystalline material is stochi-
ometric $As_2Te_3$.

The results of the above studies are pertinent to an explanation
of the observed phenomena in the present material. The initial
high resistance of the sample corresponds to the glassy state.
As the voltage across the material increases, heating effects
cause a considerable increase in the internal temperature of the
material. In contrast to other materials reported, the tempera-
ture rise in 80 $As_2Te_3$:20 $As_2Se_3$ before switching may well be
sufficient to reach the crystallization point of the material.
This possibility is borne out by the unusually long switching
delay times found in this material. Initial crystallization will
be localized, and will be accompanied by a reduction in the volt-
age across the sample and a corresponding increase in the local
current through the small crystalline area. The enhancement of
current due to localization will more than offset the drop in
voltage, the power dissipation will increase, and the crystalli-
zation will continue. This process is regenerative in nature
and corresponds to the first region of the negative resistance
characteristic shown in Figure 2. The temperature is increasing
as the sample moves back along this negative resistance line,
and eventually the liquefication point is reached. This tran-
sition is endothermic or heat absorbing and tends to considerably
slow the regenerative process until finally the sample approaches
a stable temperature situation and the runaway ceases. The onset
of liquefication corresponds to the beginning of the second re-
gion of negative resistance. As the sample is cooled from the
liquid state, it may return to the glassy, high resistance state
or the crystalline, low resistance state, depending upon the rate
of cooling. These are the situations corresponding to the sweeps
of Figures 2 and 3, respectively.

## CONCLUSIONS

The I-V characteristics of 80 $As_2Te_3$:20 $As_2Se_3$ have been explained

in terms of thermal heating which leads to successive crystallization and liquefication of a localized region of the bulk sample. The breakdown voltage of the material was found to be essentially independent of the sample thickness.

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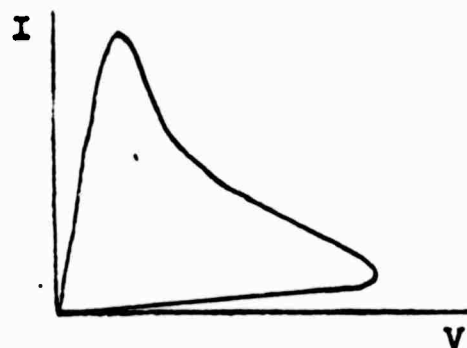Fig. 1 High resistance state



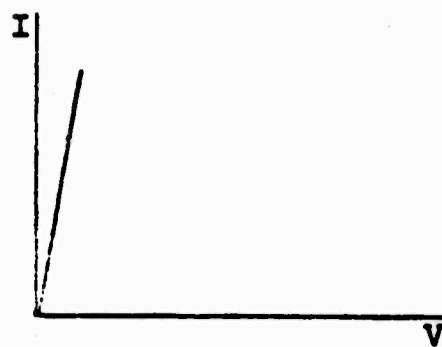Fig. 2　Threshold switching



Fig. 3　Memory cycle
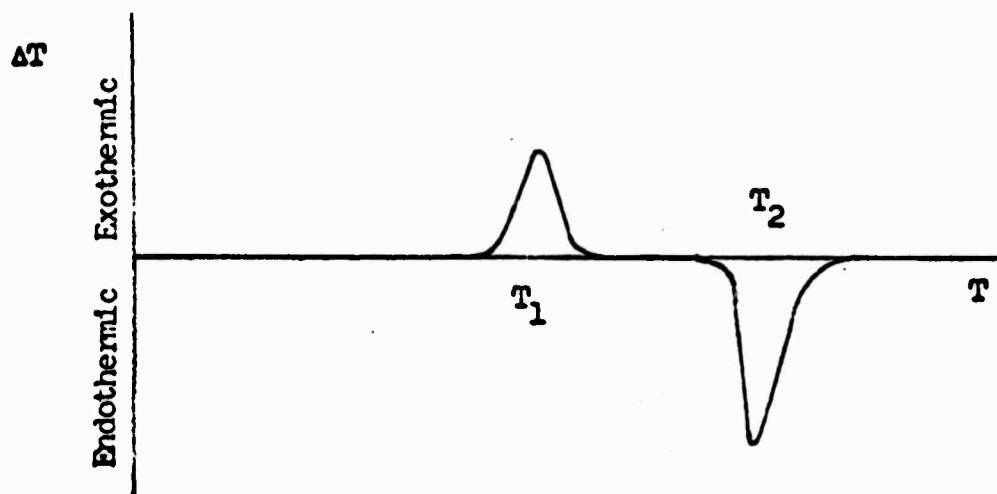


Fig. 4　Low resistance state



Fig. 5　D.T.A. Thermogram for a GeAsTe glass

ANTIFERROMAGNETISM IN AN OXIDE SEMICONDUCTING GLASS

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ANTIFERROMAGNETISM IN AN OXIDE SEMICONDUCTING GLASS

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## Abstract

The magnetic structure of a 55 mole % FeO – 45 mole % $P_2O_5$ semiconducting glass containing various relative concentrations of $Fe^{3+}$ and $Fe^{2+}$ has been studied by ESR techniques over the temperature range –192 to 300°C. It was determined that the iron ions in the glass matrix are antiferromagnetically coupled in $Fe^{3+}$ – $Fe^{2+}$ ion pairs. The isolated $Fe^{3+}$ ions were found to be in orthorhombic crystalline fields with $\lambda = 1/3$ and $0.23 < D < 0.8$ $cm^{-1}$, where D and $\lambda$ are constants in the spin Hamiltonian. Heat treatment of the glass samples caused precipitation of $Fe^{3+}$ -rich crystalline phases, and it was determined that the $Fe^{3+}$ ions in these phases were antiferromagnetically aligned.

Die magentische Struktur eines 55 mole % FeO – 45 mole % $P_2O_5$ Halbleiterglases, welches verschiedene Konzentrationen von $Fe^{3+}$ und $Fe^{2+}$ aufwies, wurde im ESR-Verfahren innerhalb der Temperaturspanne von –192 bis 300°C untersucht. Es stellte sich heraus, dass die Eisenionen im Glas in antiferromagnetischen $Fe^{3+}$ – $Fe^{2+}$ – Paaren auftreten. Die isolierten $Fe^{3+}$ -Ionen traten in orthorhombischen Kristallfeldern mit $\lambda = 1/3$ und $0.23 < D < 0.8$ $cm^{-1}$ auf, wo D und $\lambda$ Konstanten in der Hamiltonischen Drehung sind. Erhitzung des Glases rief $Fe^{3+}$ – reichen Kristallniederschlag hervor,

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1

und es wurde festgestellt, dass die $Fe^{3+}$ - Ionen im Niederschlag antiferro-
magnetisch ausgerichtet sind.

## 1. Introduction

The study of the magnetic properties of transition metal and rare earth
ions in amorphous hosts is a relatively new field, which was pioneered by
Sands (1), who employed electron spin resonance techniques to study ions in
glassy hosts. Various investigators have attempted to elucidate the role of
isolated metal ions, such as iron, in glass (2-10). However, with the ex-
ception of the vanadium-phosphate system, few glasses with a high concentra-
tion of the metal ion have been thoroughly investigated (1).

Various investigators have begun to study the electrical and magnetic
properties of the iron-phosphate glass system. The electrical conductivity
of a 55 mole % FeO - 45 mole % $P_2O_5$ glass has been studied (12-18), and there
has been a report of correlations between the electrical and magnetic properties
of the glass (19). The purpose of this paper is to more fully investigate and
characterize the magnetic structure of this glass.

## 2. Experimental

The glass samples were prepared by melting a physical mixture of $Fe_2O_3$
and $P_2O_5$ in air at 1300°C for one hour, quenching to room temperature, and
annealing for one hour at 300°C. To obtain various relative concentrations
of $Fe^{3+}$ and $Fe^{2+}$, dextrose was added to the melt. The concentration of the
total iron and the relative concentrations of $Fe^{3+}$ and $Fe^{2+}$ were de-
termined by chemical analysis. The glass samples studied contained 55 mole
% FeO and 45 mole % $P_2O_5$. The relative concentrations of $Fe^{3+}$ to total iron
($Fe^{3+}$/Fe) were 75, 45, and 30%. The samples were heat-treated in air for
one hour at 400, 500, 600, 700, and 750°C. Weighed, powdered samples were
used for ESR measurements.

und es wurde festgestellt, dass die $Fe^{3+}$ - Ionen im Niederschlag antiferro-
magnetisch ausgerichtet sind.

## 1. Introduction

The study of the magnetic properties of transition metal and rare earth
ions in amorphous hosts is a relatively new field, which was pioneered by
Sands (1), who employed electron spin resonance techniques to study ions in
glassy hosts. Various investigators have attempted to elucidate the role of
isolated metal ions, such as iron, in glass (2-10). However, with the ex-
ception of the vanadium-phosphate system, few glasses with a high concentra-
tion of the metal ion have been thoroughly investigated (1).

Various investigators have begun to study the electrical and magnetic
properties of the iron-phosphate glass system. The electrical conductivity
of a 55 mole % FeO – 45 mole % $P_2O_5$ glass has been studied (12-18), and there
has been a report of correlations between the electrical and magnetic properties
of the glass (19). The purpose of this paper is to more fully investigate and
characterize the magnetic structure of this glass.

## 2. Experimental

The glass samples were prepared by melting a physical mixture of $Fe_2O_3$
and $P_2O_5$ in air at 1300°C for one hour, quenching to room temperature, and
annealing for one hour at 300°C. To obtain various relative concentrations
of $Fe^{3+}$ and $Fe^{2+}$, dextrose was added to the melt. The concentration of the
total iron and the relative concentrations of $Fe^{3+}$ and $Fe^{2+}$ were de-
termined by chemical analysis. The glass samples studied contained 55 mole
% FeO and 45 mole % $P_2O_5$. The relative concentrations of $Fe^{3+}$ to total iron
($Fe^{3+}$/Fe) were 75, 45, and 30%. The samples were heat-treated in air for
one hour at 400, 500, 600, 700, and 750°C. Weighed, powdered samples were
used for ESR measurements.

ESR studies were made on a laboratory spectrometer at 9 GHz. Magnetic field strength was determined by means of a proton spin resonance gaussmeter, and the klystron frequency was measured by a direct reading hetrodyne frequency counter.

To determine the spin density of each resonance line and to study the intensity of the line as a function of experiment temperature, it was necessary to calculate the area under the absorption curve. In terms of the first derivative line, $I \sim \Delta H^2 h_{pp}$, where $\Delta H$ is the linewidth and $h_{pp}$ is the peak-to-peak height of the first derivative spectra (20). The spin density of the iron contributing to the resonance line was determined by comparison with a calibrated sample. Likewise, the normalized intensity of the ESR lines was determined. The intensity of the glass line was divided by the intensity of a paramagnetic standard (DPPH) in order to remove the temperature dependence of the sensitivity of the spectrometer (21, 22).

Finely powdered glass samples were examined in a vacuum Guinier-DeWolff X-ray camera using Mo K$\alpha$ radiation. This technique permitted detection and identification of as little as 0.1 wt% crystal.

### 3. Results and Discussion

The electron spin resonance spectra of the 55-45 mole % $FeO-P_2O_5$ glasses consists of three sets of resonance lines: weak resonances at $g'=2.00$, 4.28, and 6 attributed to isolated $Fe^{3+}$ ions in a crystalline field, a broad resonance centered at $g' = 2.01$ arising from antiferromagnetically coupled $Fe^{2+}-Fe^{3+}$ ion pairs, and a singlet centered at $g' = 2.00$, which is evidence of devitrification in the glass samples.

Resonance lines at $g' = 0.86$, 2.00, 4.28, 6 and 11 are typical of isolated $Fe^{3+}$ in crystalline fields of symmetry lower than cubic. The resonances at $g' = 0.86$ and 11 should be weak compared to the resonance at $g' = 4.28$ if the crystalline field is such that the former lines arise from transitions

within a Kramer's doublet of higher energy than the Kramer's doublet which gives rise to the $g' = 4.28$ line. It can be seen in Figure 1 that such is the case in the as-cast glass containing 75% $Fe^{3+}$/Fe. Figure 2 is an enlargement of the region around $g' = 2$ for the spectra at $-196°C$.

The doublet shown here has been tentatively identified as the $1/2 - 1/2$ and $3/2 - 1/2$ transitions. The breadth of the high field line is probably a result of exchange coupling and inhomogeneity broadening, as discussed below.

Approximate values of the crystalline field parameters, D and $\lambda = E/D$, of the spin Hamiltonian for iron in a crystalline field,

$$H = g\mu\overline{H}\cdot\overline{S} + D[S_z^2 - 1/3S(S+1)] + E[S_x^2 - S_y^2],$$

can be determined by comparison of ESR spectra run at 9 and 35 GHz. The $g' = 4.28$ line, which is evident in the 9 GHz spectra, is absent in the 35 GHz spectra at room temperature. The crystalline field resonances at $g' = 2.00$ and 6 are observable only at liquid nitrogen temperature; their presence or absence at 35 GHz could not be determined from the room temperature spectra. However, based on the behavior of the line at $g' = 4.28$, one can approximate the values of D and $\lambda$ using the method of Downsing and Gibson (3). The $Fe^{3+}$ ions are determined to be in orthorhombic crystalline fields with $\lambda \approx 1/3$ and $0.23 < D < 0.8$ cm$^{-1}$.

Measurements of spin density were performed on the glass samples, and it was found that only one part in $10^8$ of the $Fe^{3+}$ present in the glass contributed to the $g' = 4.28$ resonance line. This striking result may be explained in terms of antiferromagnetic coupling of the $Fe^{3+}$ ions. If almost all of the $Fe^{3+}$ ions in the glass are antiferromagnetically coupled, only a small fraction would behave as isolated ions; and this small fraction cannot be considered as totally isolated. Plots of linewidth of the $g' = 4.28$ line as a function of experiment temperature show a general increase in linewidth as the temperature decreases. This may be interpreted in terms of spin-spin relaxation, rather

than spin-lattice relaxation which would cause the opposite temperature dependence. Hence, even the isolated $Fe^{3+}$ ions in the glass, which give rise to the crystalline field resonances, are subject to exchange interactions.

In addition to the crystalline field lines, the ESR spectra of all glass samples contains a very broad, symmetric resonance centered at $g' = 2.01$. In the as-cast glasses, the linewidth of this resonance is greater than 10,000 gauss. However, as can be seen in Figure 3, the linewidth decreases for samples heat-treated at temperatures up to 700°C. This behavior can be interpreted in terms of devitrification of the glass and growth of $Fe_3O_4$ and $FePO_4$ crystalline phases. Van Vleck (23) has shown that exchange interaction between ions in different valence states results in a broadening of the resonance line. As devitrification of the matrix occurs and the crystalline phases form, the $Fe^{3+}$ concentration in the matrix decreases more rapidly than the $Fe^{2+}$ concentration; the exchange interaction between $Fe^{2+}$ and $Fe^{3+}$ ions in the matrix decreases, and the breadth of the line decreases. As the glass is heat-treated near its melting point, as in the case of the sample heat-treated at 750°C, order in the glass matrix is reduced, and there is greater site-to-site variation. Increased solubility of the crystalline phase at higher temperatures allows more of the iron ions to return to the glass matrix; exchange and inhomogeneity broadening begin to once again broaden the resonance line.

The intensity of the broad line centered at $g' = 2.01$ was measured as a function of experiment temperature in the as-cast and heat-treated glasses. This result is shown in Figure 4. The normalized intensity of this line generally increases as the experiment temperature decreases. Likewise, as seen in Figure 5, the linewidth increases as the temperature decreases, indicating the presence of spin-spin relaxation as discussed above. The scatter in the data shown in Figures 4 and 5 is probably the result of the approximations made in measuring linewidths and peak-to-peak heights from the spectra. Because the low field peak was obscured by the $g' = 4.28$ line, it was necessary

to make all measurements on the high field peak and then double them. Noise and the extreme broadness of the line may have introduced random errors into the measurements.

A possible origin for the anomalies in the data shown in Figures 4 and 5 may be found in the work of Wilson and Kinser (24), who proposed that antiferromagnetic transitions corresponding to those in the pure phase metal oxides could occur in the glassy matrix. However, the possibility of error in these measurements makes it difficult to employ such a theory in this case.

The temperature dependence of the intensity is the result of the exchange coupling between iron ions. Owen (25, 26) has derived the following Hamiltonian for the exchange interactions between the $i^{th}$ and $j^{th}$ ion:

$$H_{ex} = J \ S^i \cdot S^j + D_{ex}(3S_z^i S_z^j - S^i \cdot S^j) + E_{ex}(S_x^i S_x^j - S_y^i S_y^j)$$

This includes the dipole-dipole term $D_d = -q^2\beta^2/r^3_{ij}$ in the constant $D_{ex} = D_d + D_E$, where $D_E$ is the anisotropic exchange term. As Owen points out, the anisotropic term is of low order and smaller than $D_d$, so that it acts only as a perturbation on the first term in J. The term in J is the exchange term and creates states of total angular momentum S, which follow the Lande interval rule.

If J is positive, the exchange will be antiferromagnetic, and the resonance will have a characteristic temperature dependence. If the exchange is between $Fe^{3+}$ ions, the ground state will have total spin S = 0, and the normalized intensity of the ESR line will decrease as T decreases, following a Boltzmann distribution (22):

$$\frac{I}{I_o} = \frac{\sum_{S=0}^{5} 2S \ \exp \ [-S(S+1)J/2kT]}{\sum_{S=0}^{5} (2S+1)\exp[-S(S+1)J/2kT]}$$

On the other hand, if the exchange is antiferromagnetic and between $Fe^{3+}$ and $Fe^{2+}$ ions, the ground state will have total spin S = 1/2, and the normalized intensity will increase as the temperature decreases (25).

The line intensity of the broad resonance centered at $g' = 2.01$ increases as the temperature decreases, indicating antiferromagnetic coupling between $Fe^{3+}$ and $Fe^{2+}$ ions. Evidence for this antiferromagnetic exchange coupling between the iron ions of different valence state is also found upon comparison of the ESR spectra of samples containing different relative concentrations of $Fe^{3+}/Fe$. In the spectra of the as-cast glasses containing 75 and 30% $Fe^{3+}/Fe$, the linewidth of the resonance is less than in the spectrum of the 45% $Fe^{3+}/Fe$ glass. This result is in accord with Van Vleck (23), since in the 45% $Fe^{3+}/Fe$ glass there is an almost equal concentration of $Fe^{3+}$ and $Fe^{2+}$ ions. Hence the exchange broadening should be the greatest in this case. Indeed, this is so.

Magnetic susceptibility measurements have been made on all glass samples (27). All samples obey a Curie Weiss law and exhibit weak ferromagnetism with $T_c \simeq 120°K$ and $J \simeq 1 \text{ cm}^{-1}$. The bulk behavior is consistent with the proposed antiferromagnetic coupling between the iron ions, which has been observed in magnetic resonance experiments. Antiferromagnetic coupling between $Fe^{3+}$ and $Fe^{2+}$ ions in the glassy matrix results in a net magnetic moment for each pair of spins. The resultant moments are randomly oriented throughout the matrix, and thus the glass remains paramagnetic over the temperature region studied.

Certainly, one can rule out the possibility of ferromagnetic coupling between individual spins. With such a large quantity of iron in the sample, ferromagnetic coupling would lead to extremely strong resonances and would be in conflict with the susceptibility data. Therefore, a reasonable magnetic model for the as-cast glass is one in which there is extensive antiferromagnetic coupling between $Fe^{3+}$ and $Fe^{2+}$ ions with a slight resultant magnetization such that the glass displays weak bulk ferromagnetism below $T_c$.

Thermal treatment of the glass at temperatures above 400°C causes some devitrification. As seen in Figure 6, the ESR spectra of the heat-treated

samples contains a large singlet of approximately 200 gauss linewidth centered at $g' = 2.00$. This singlet is apparently associated with the growth of crystalline phases which have been detected in these samples by X-ray and electron microscopy techniques.

X-ray analysis has shown that during heat treatment various $Fe^{3+}$-rich crystalline phases precipitate from the glass matrix. As shown in Table 1, heat treatment of the glass samples at 600°C for one hour results in the growth of $FePO_4$ and $Fe_3O_4$. Samples heat-treated for 10 hours at 600°C show

TABLE I

| Heat Treatment | Crystalline Phases Detected |
| --- | --- |
| 1 Hour at 600°C | $Fe_3O_4$, $FePO_4$ |
| 10 Hours at 600°C | $Fe_3O_4$, $FePO_4$ |
| 14 Hours at 800°C | $Fe_3O_4$, $FePO_4$, $Fe_3PO_7$, $Fe_4(P_2O_7)_3$ |

continued growth of the same phases. However, the X-ray spectra of samples heat-treated at 800°C for 14 hours shows evidence of $Fe_3O_4$ and $FePO_4$ and also lines which may be attributed to $Fe_4(P_2O_7)_3$ and $Fe_3PO_7$. It is apparent that heat treatment at this elevated temperature enhances combination of $Fe_3O_4$ into iron-phosphate complexes (28).

One may interpret the existence of the singlet at $g' = 2.00$ in the ESR data as evidence of $Fe^{3+}$-rich crystalline phases. Since $Fe_3O_4$ contains two trivalent ions for every divalent one, and since $Fe^{3+}$ ions are also incorporated into the $FePO_4$ crystallites, the observed resonance is primarily due to the precipitated $Fe^{3+}$ ions. Furthermore, the absolute intensity of this resonance line follows the ratio 0.75 : 0.45 : 0.29 for glass samples containing 0.75 : 0.45 : 0.30 $Fe^{3+}/Fe$, respectively. Thus, it has been concluded that the singlet at $g' = 2.00$ is associated with the $Fe^{3+}$-rich crystalline phases.

The linewidth and normalized intensity of the $g' = 2.00$ singlet observed in glasses heat-treated at 600°C for one hour have been studied as a function

of experiment temperature, and these results appear in Figures 7 and 8. In general, the linewidth increases as the temperature decreases, which is again indicative of spin-spin relaxation. The normalized intensity also increases as the temperature decreases to approximately -100°C in the case of 75% $Fe^{3+}$/Fe sample. Here the intensity levels off and then decreases, which is evidence of an antiferromagnetic transition temperature of about -120°C. Similar behavior is noted in the sample containing 45% $Fe^{3+}$/Fe, but here the transition temperature is at a lower temperature, about -160°C. In the sample containing 30% $Fe^{3+}$/Fe, the transition temperature is below -196°C.

If most of the $Fe^{3+}$ ions in the segregated crystalline phases are aligned antiferromagnetically, this would account for the observed temperature dependence of the intensity of the g' = 2.00 line. In the region above the transition temperature, there is a slight non-colinearization of the spins of each pair. As the temperature is decreased towards the transition temperature, thermal population of the higher $M_S$ states in each spin manifold decreases. Since the ESR line intensity for any $\Delta M_S = \pm 1$ transition is proportional to the difference in population between the $M_S$ and the $M_{S+1}$ levels, the intensity increases. At the transition temperature, the individual $Fe^{3+}$ ions in each pair align antiferromagnetically, which causes the net pair magnetic moment to drop. The line intensity then decreases as the temperature is lowered. This behavior is never noted in the case of the g' = 2.01 line since there is always a resultant magnetic moment from the $Fe^{3+}$ - $Fe^{2+}$ exchange interaction. Even in the case of the coupled spins in the crystalline phases there will be a resultant magnetic moment from the $Fe_3O_4$. Nevertheless, there is an antiferromagnetic alignment of the spins in the other crystalline phases, and the antiferromagnetic transition in these phases causes the reduction of the line intensity.

As the $Fe^{3+}$/Fe ratio decreases, and hence as the $Fe^{3+}$ concentration decreases the average $Fe^{3+}$ - $Fe^{3+}$ interaction distance increases. This causes a decrease

in the exchange integral J and a corresponding decrease in the transition
temperature as noted above.

## 4. Summary

In conclusion, ESR studies of a 55 mole % FeO, 45 mole % $P_2O_5$ glass with
varying relative concentrations of $Fe^{3+}$ and $Fe^{2+}$ have determined that most of
the iron in the glassy matrix is highly coupled in $Fe^{3+}$ - $Fe^{2+}$ ion pairs.
These antiferromagnetically coupled pairs have a net residual magnetic moment,
and the glass displays weak ferromagnetic behavior in magnetic susceptibility
measurements. The $Fe^{3+}$ ions in the glass have been determined to be in ortho-
rhombic fields with $\lambda \simeq 1/3$ and $0.23 < D < 0.8$ cm$^{-1}$.

Heat treatment of the glass above 400°C causes devitrification and sepa-
ration of $Fe^{3+}$ -rich crystalline phases which have been identified as $Fe_3O_4$,
$FePO_4$, $Fe_3PO_7$, and $Fe_4(P_2O_7)_3$. The $Fe^{3+}$ ions in these crystalline phases are
also antiferromagnetically coupled, and show antiferromagnetic resonance with
a transition temperature of about -120°C in the case of the 75% $Fe^{3+}$/Fe glass,
about -160°C in the case of the 45% $Fe^{3+}$/Fe glass, and below -196°C in the
case of the 30% $Fe^{3+}$/Fe glass.

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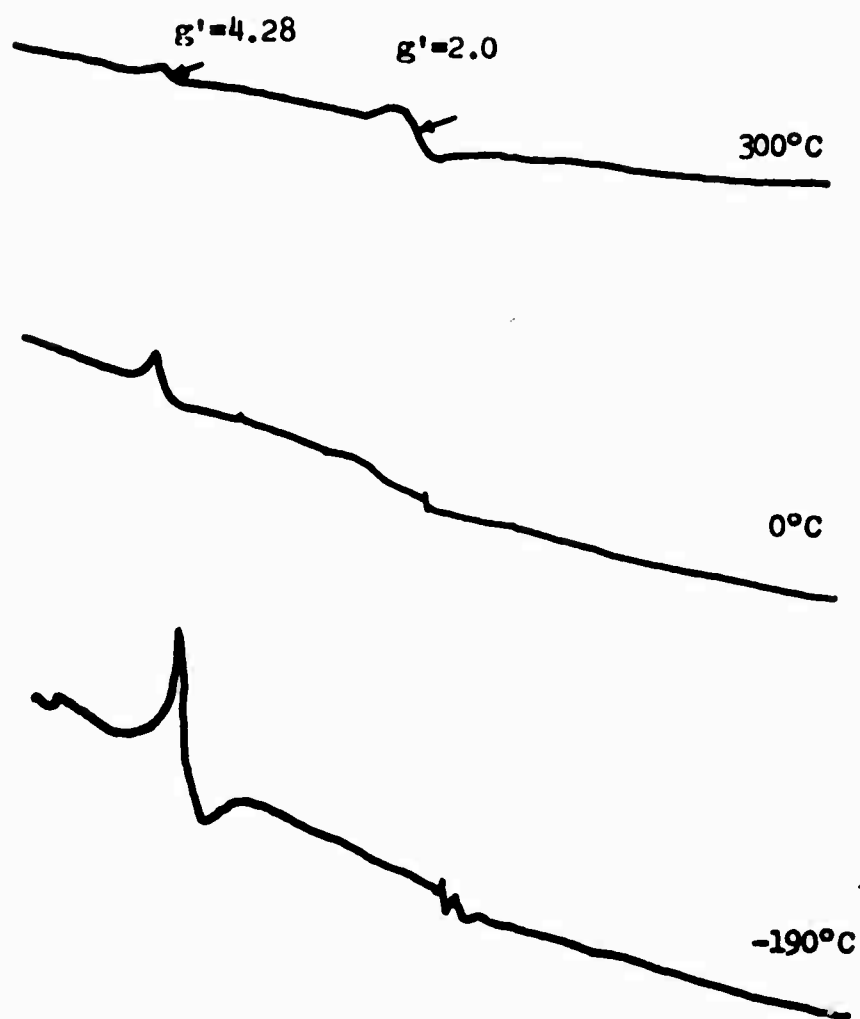# FIGURES

1. ESR Spectra of 75% $Fe^{3+}$/Fe Glass Sample After Annealing for One Hour at 300°C. $\nu$ = 9.160 GHz.

2. ESR Spectra of 75% $Fe^{3+}$/Fe Sample Annealed for One Hour at 300°C.

3. ESR Linewidth of the g' = 2.01 Line <u>VS</u>. Annealing Temperature for 75% $Fe^{3+}$/Fe Glass Samples Annealed at 300°C for One Hour.

4. Normalized Intensity of the g' = 2.01 ESR Line as a Function of Experiment Temperature for a Glass Sample Containing 30% $Fe^{3+}$/Fe Which Had Been Heat-Treated for One Hour at 600°C.

5. ESR Linewidth of the g' = 2.01 Line as a Function of Experiment Temperature for a Glass Sample Containing 30% $Fe^{3+}$/Fe Which Had Been Heat-Treated for One Hour at 600°C.

6. Effect on ESR Spectra of Heat Treating 75% $Fe^{3+}$/Fe Samples for One Hour. $\nu$ = 9.160 GHz.

7. ESR Linewidth of the g' = 2.00 Line as a Function of Experiment Temperature for Glass Samples Heat-Treated at 600°C for One Hour.

8. Normalized Intensity of the g' = 2.00 ESR Line as a Function of Experiment Temperature for Glasses Heat-Treated for One Hour at 600°C.

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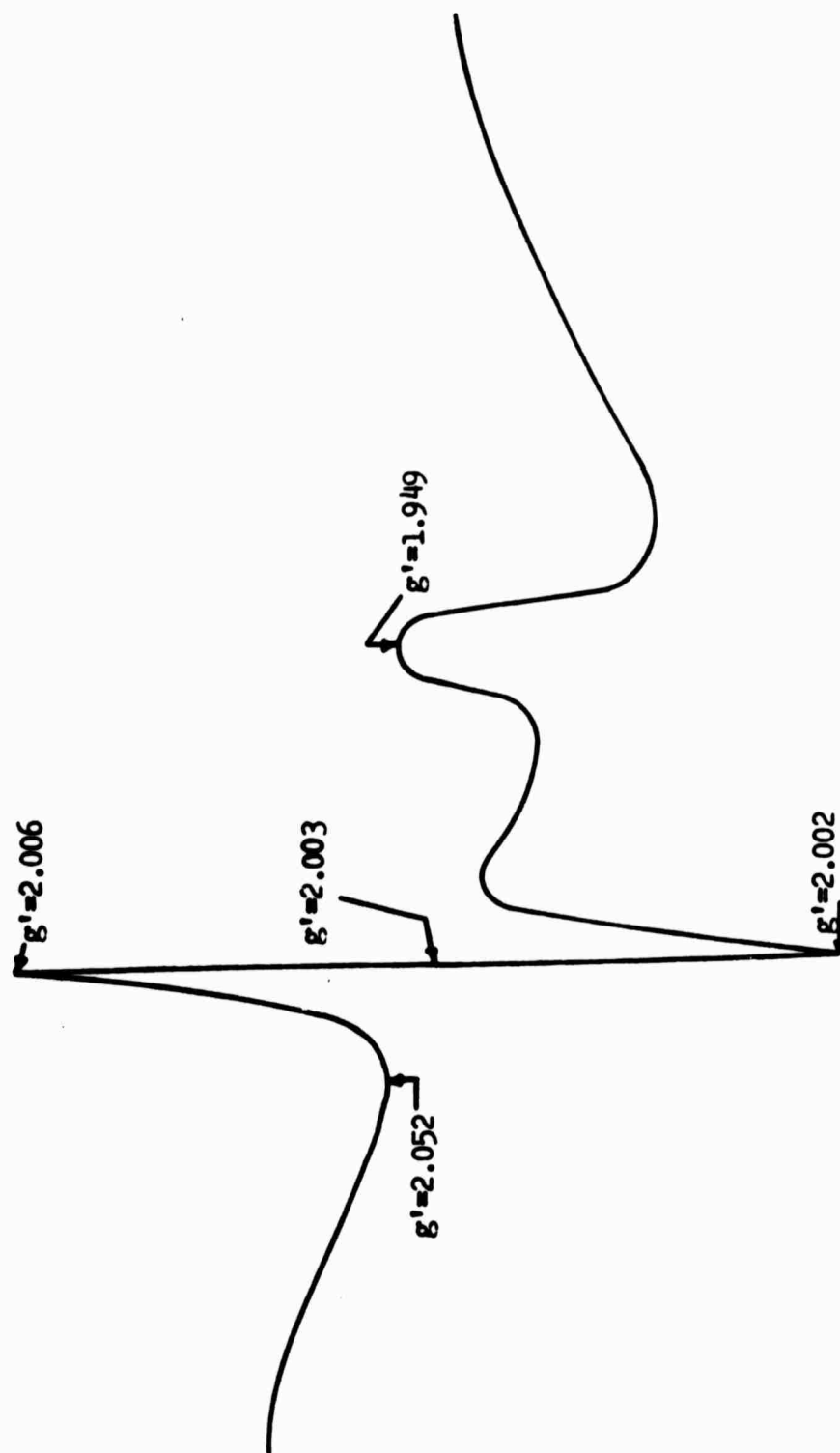FIGURE 1. ESR Spectra of 75% $Fe^{3+}$/Fe Glass Sample After Annealing for One Hour at 300°C. $\nu = 9.160$ GHz.

FIGURE 2. ESR Spectra of 75% $Fe^{3+}$/Fe Sample Annealed for One Hour at 300°C.
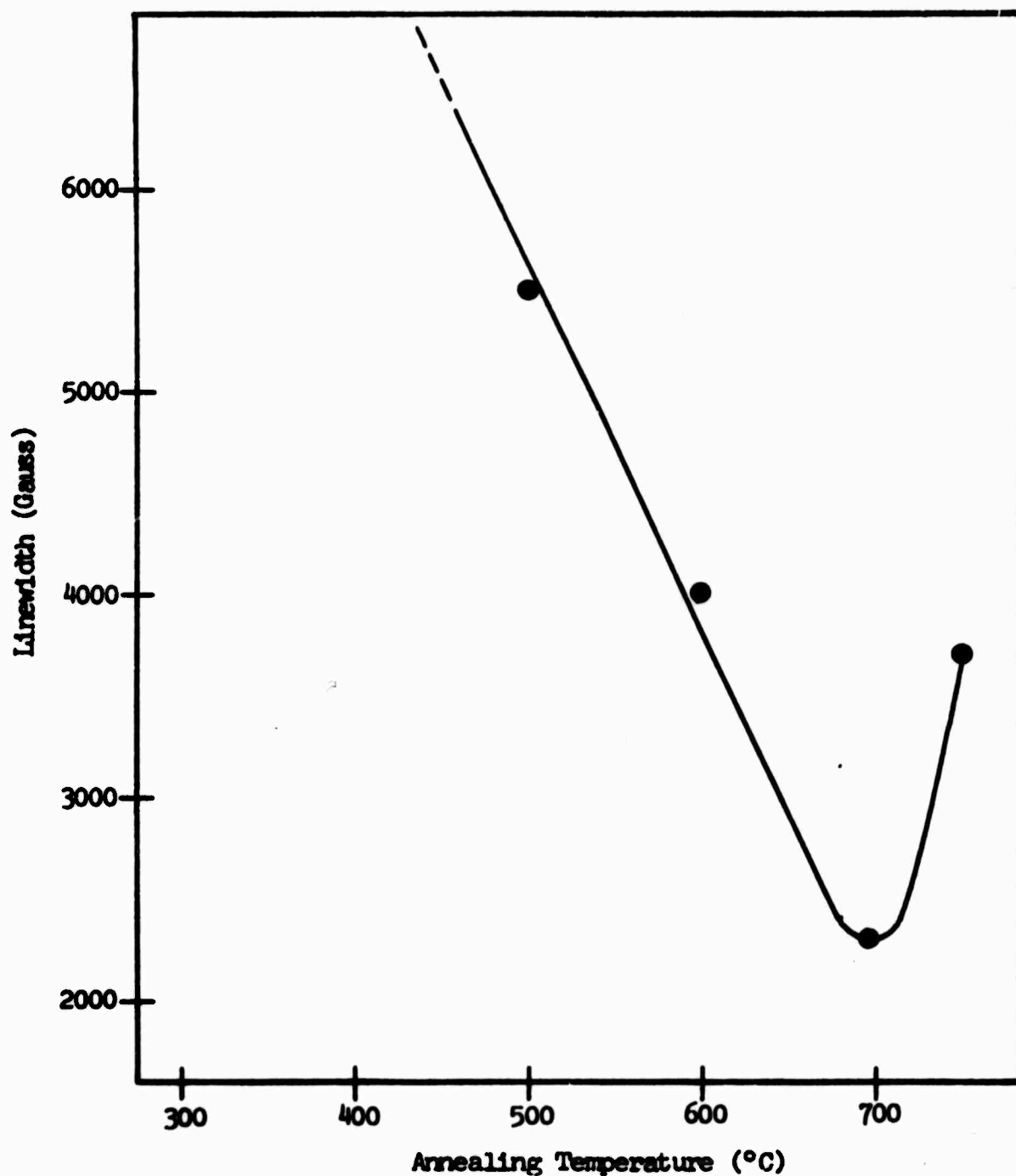
FIGURE 3. ESR Linewidth of the $g'=2.01$ Line VS. Annealing Temperature for 75% $Fe^{3+}/Fe$ Glass Samples Annealed at 300°C for One Hour.

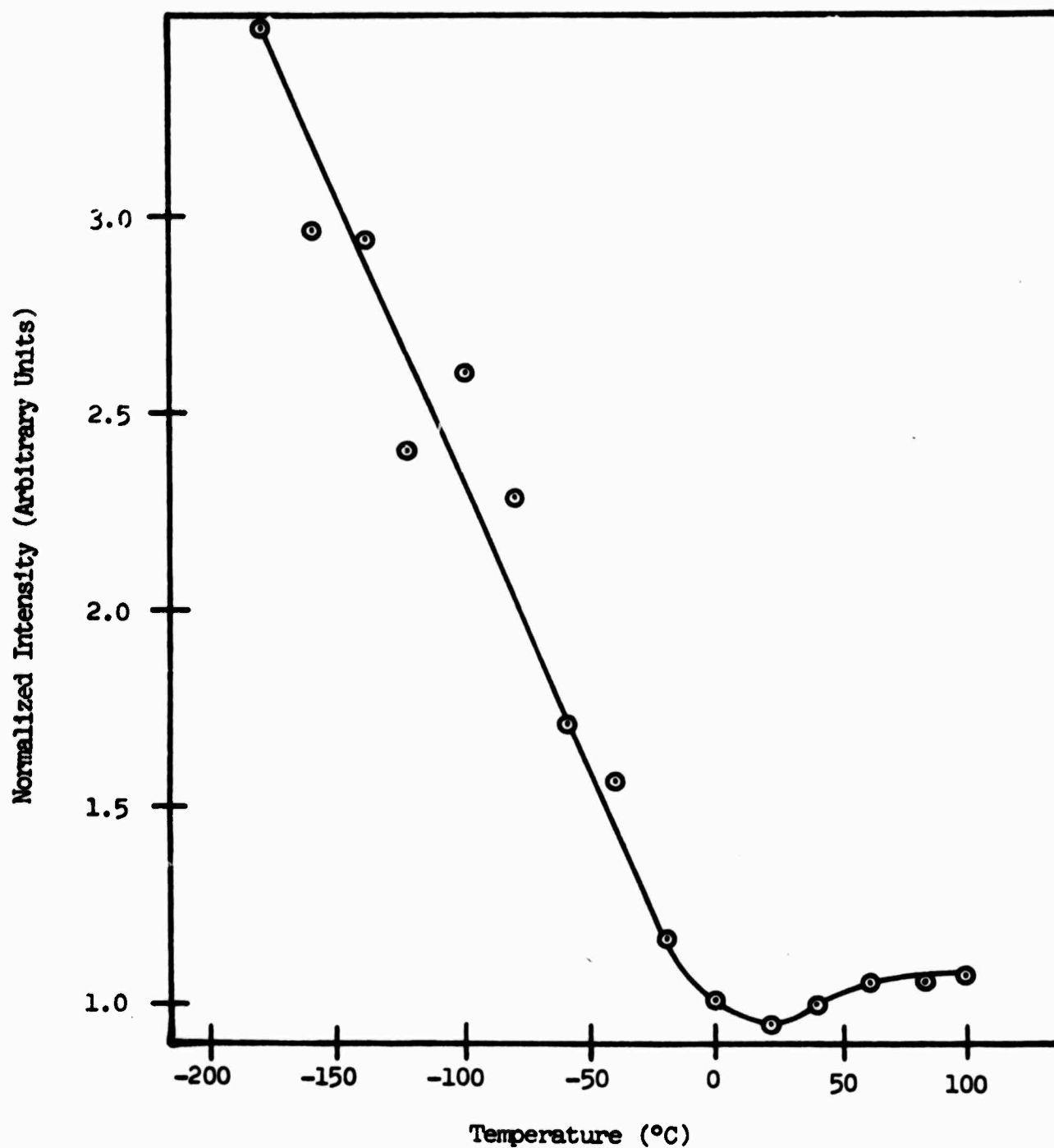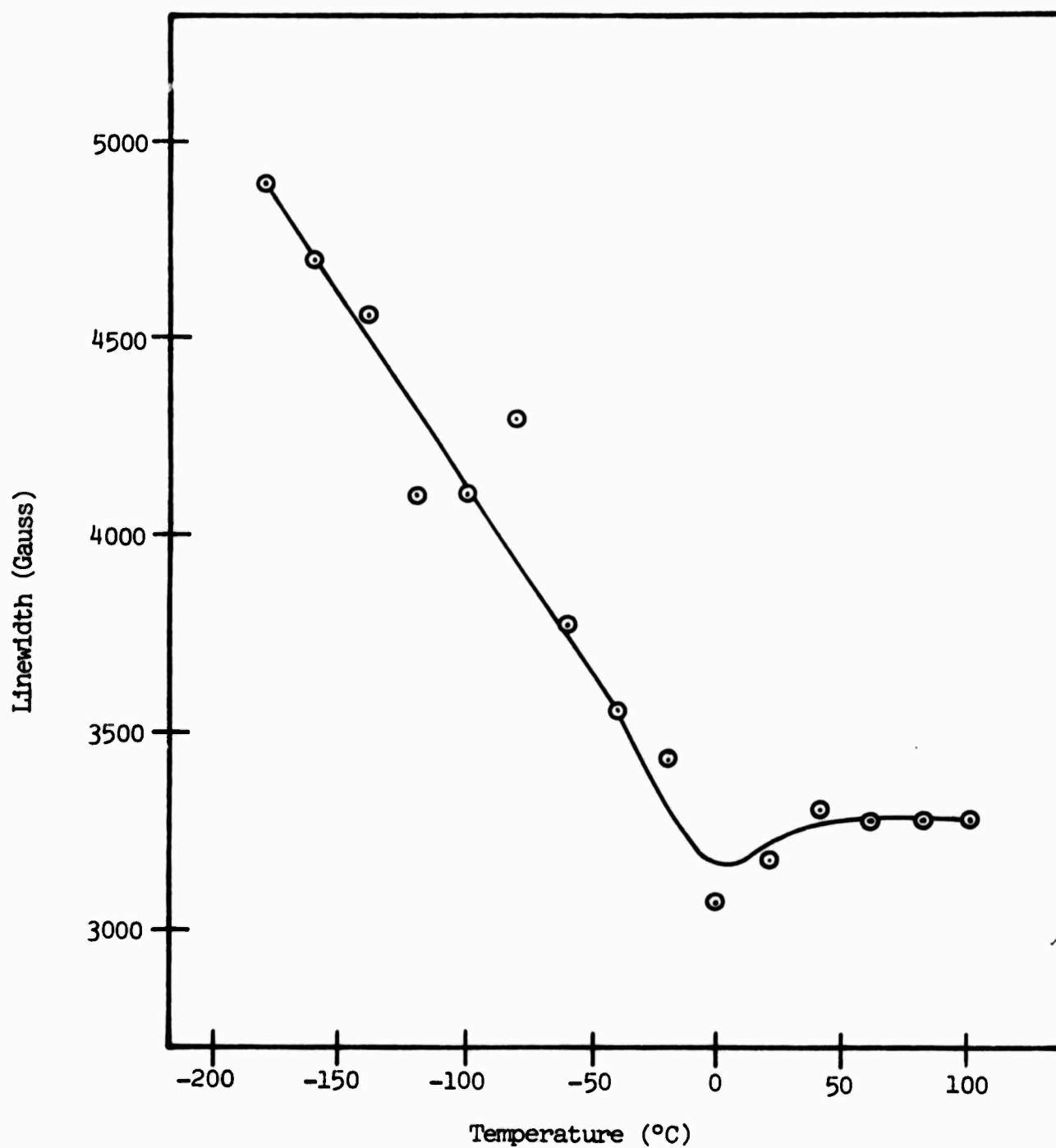FIGURE 4. Normalized Intensity of the g'=2.01 ESR Line as a
Function of Experiment Temperature for a Glass Sample
Containing 30% $Fe^{3+}$/Fe Which Had Been Heat-Treated
For One Hour at 600°C.

FIGURE 5. ESR Linewidth of the $g'=2.01$ Line as a Function of Experiment Temperature for a Glass Sample Containing 30% $Fe^{3+}$/Fe Which Had Been Heat-Treated For One Hour at 600°C.
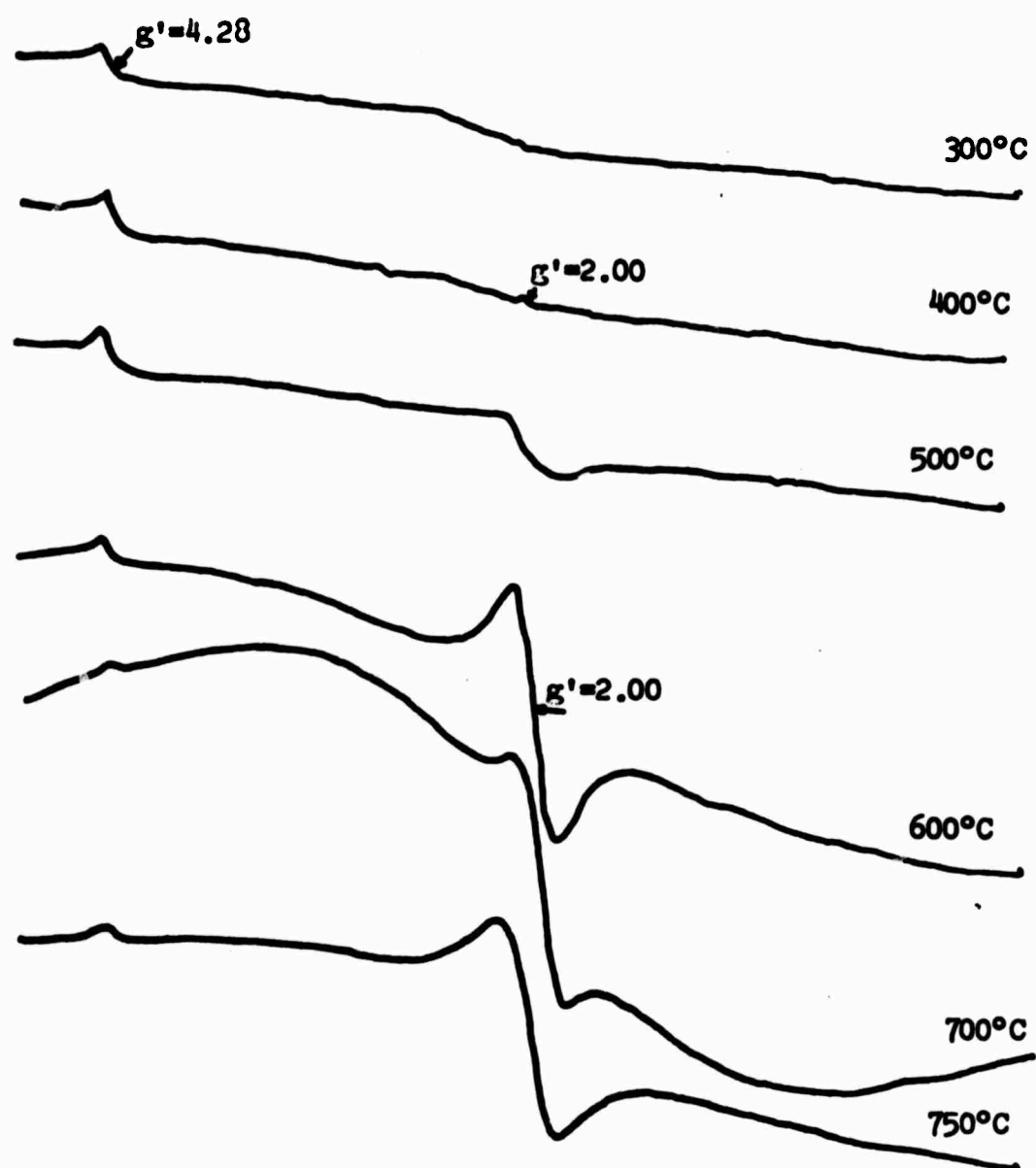
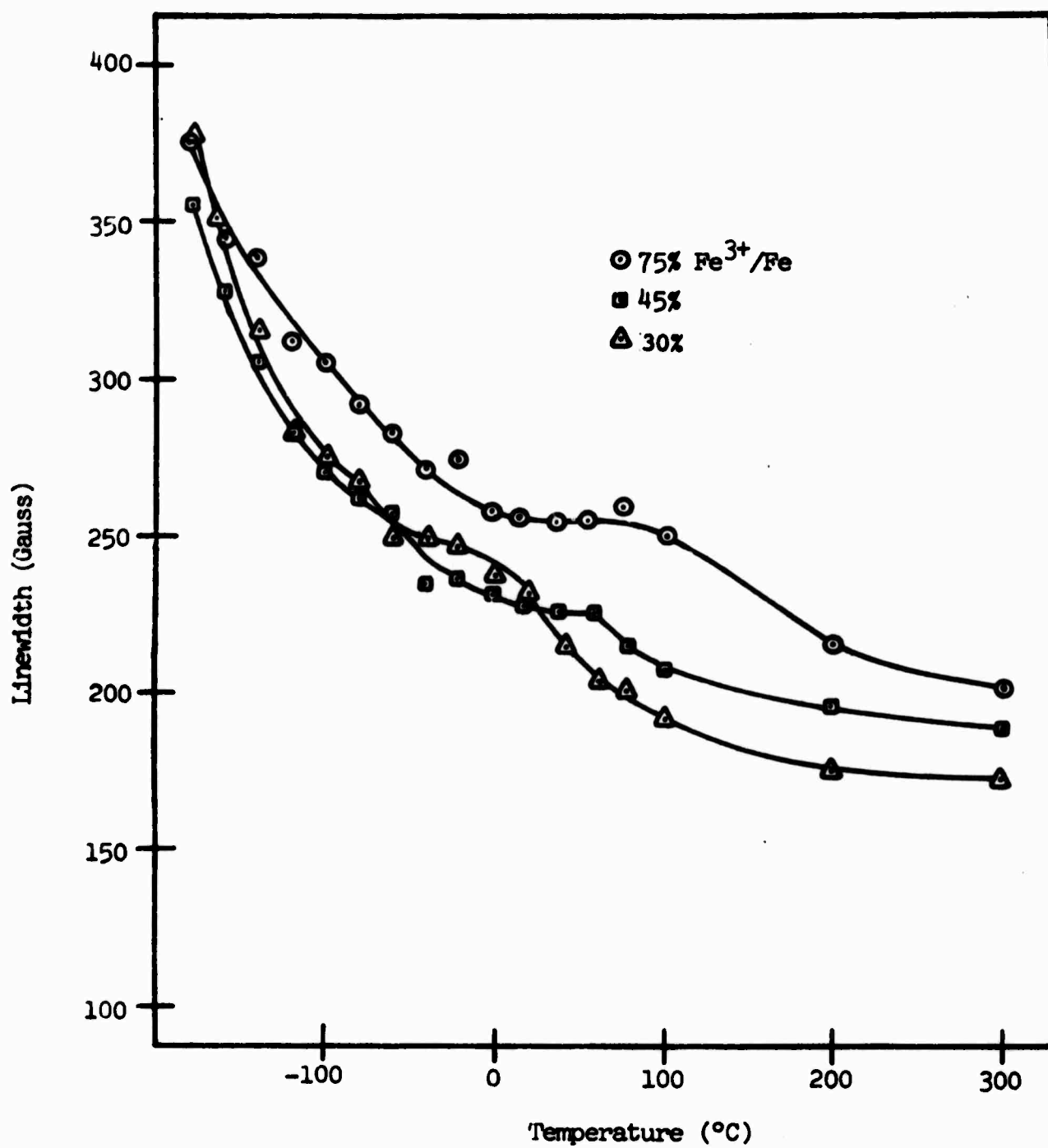FIGURE 6. Effect on ESR Spectra of Heat Treating 75% $Fe^{3+}$/Fe Samples for One Hour. $v$=9.160 GHz.

FIGURE 7. ESR Linewidth of the $g' = 2.00$ Line as a Function of Experiment Temperature for Glass Samples Heat-Treated at 600°C for One Hour.
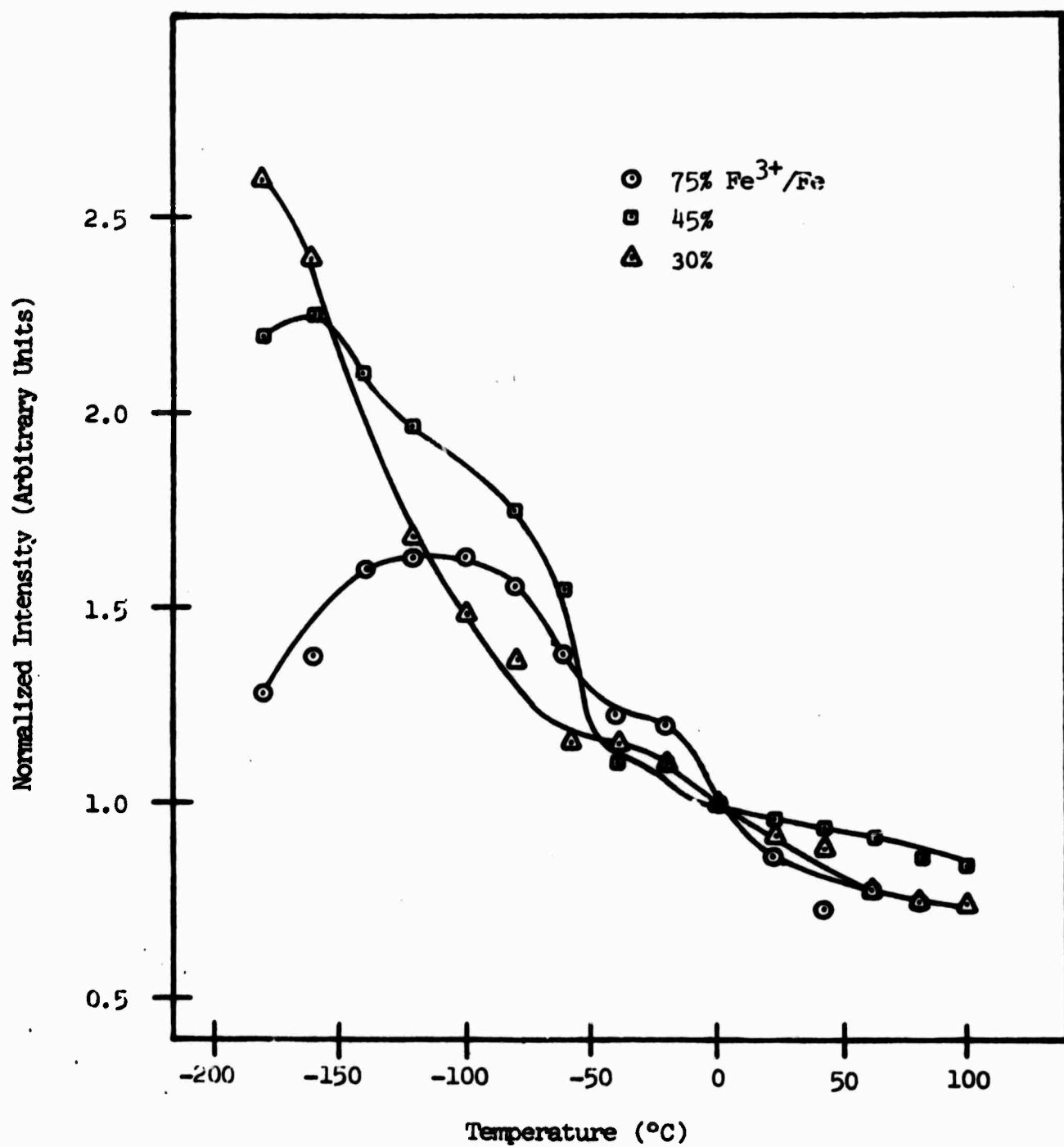
FIGURE 8. Normalized Intensity of the g'=2.00 ESR Line as a
Function of Experiment Temperature for Glasses
Heat-Treated for One Hour at 600°C.